VERIFICATION OF TRANSLATION

I, the undersigned *JAKUB SIELEWIESIUK*, residing at 87 Bema Street, apt. 129, 01-233 Warsaw, Poland
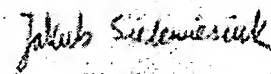
declare as follows:

1. that I am acquainted with both the English and Polish languages

and

2. that the attached document in English is a true and complete translation verified by me to the best of my knowledge and belief of:

the certified copy of the patent application No. P-357709 filed with the Patent Office of the Republic of Poland on December 11, 2002.

Warsaw, January 14, 2008

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Verified English translation from the Polish language

PATENT OFFICE OF THE REPUBLIC OF POLAND

[State emblem]

CERTIFICATE

AMMONO Sp. z o.o.

Warszawa, Poland

NICHIA CORPORATION

Anan-Shi, Japan

filed with the P a t e n t   O f f i c e   o f   t h e   R e p u b l i c   of   P o l a n d on December 11, 2002 an application for granting a patent for the invention entitled: **"Process of obtaining a complex substrate standardized with an epitaxial layer (template-type substrate) from bulk mono-crystalline gallium-containing nitride with increased heat resistance."**

The description of the invention, the claims and drawings attached to this certificate are the true copies of the documents filed along with the application on December 11, 2002.

The application was filed under number P-357709.

Warsaw, February 11, 2003

under authorization of The President

[Pressed round seal with the emblem of the Republic of Poland and a legible circumscription: URZĄD PATENT-OWY RP *1* – put on a round piece of paper attached to the ribbon.]

[illegible signature]

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I/03 - 100840

Process of obtaining a complex substrate standardized with an epitaxial layer (template-type substrate) from bulk mono-crystalline gallium-containing nitride with increased heat resistance.

The object of this invention is the process of obtaining a complex substrate standardized with an epitaxial layer (template-type substrate) from bulk mono-crystalline gallium-containing nitride with increased heat resistance by crystallization from a supercritical solution of mono-crystalline gallium-containing nitride layers and $Al_xGa_{1-x}N$ ($0<x\leq1$).

The currently used substrates for epitaxy from mono-crystalline gallium-containing nitride are usually limited to substrates from gallium nitrides obtained by crystallization from the gaseous phase. The properties of those substrates, particularly the rate of thermal destruction in the environment of depositing epitaxial layers, are sufficient for epitaxy of gallium and indium nitrides as well as mixed aluminum-indium nitrides. However, in the case of depositing aluminum nitrides or mixed aluminum-containing nitrides it is preferable to increase the temperature in which an epitaxial layer is being grown. That, however, results in a faster thermal destruction of the substrate gallium nitride, which hinders the process of obtaining high-quality epitaxial layers. Other methods of obtaining mono-crystalline gallium-containing nitrides, including mixed gallium-aluminum nitrides, have a slow rate of crystal growth, resulting in the limited availability and high price of the thus-obtained substrates for epitaxy. For example, Polish patent application no. P-347918

proposed to obtain bulk mono-crystalline nitrides by their crystallization from supercritical ammonia-containing solution. Those nitrides can also include mixed nitrides with high aluminum content, however they are obtained at a slow growth rate – many times slower than the rate of the growth method from the gaseous phase.

The authors of this invention have discovered that it was possible to significantly increase the temperature of thermal destruction in the environment of depositing epitaxial layers on the surface of the substrate for epitaxy from mono-crystalline gallium-containing nitride by depositing a layer of mono-crystalline gallium-containing nitride produced in the supercritical ammonia, and then a layer of $Al_xGa_{1-x}N$ (0<x≤1) with increased heat resistance.

The GaN obtained in the supercritical ammonia in the environment of growth from the gaseous phase undergoes some decomposition, but it was discovered that a certain specific degree of mixing with Al allows to avoid the decomposition in analogical conditions of the gaseous phase.

Therefore, the objective of this invention is to propose a process of obtaining a bulk mono-crystalline template-type substrate which would be consistent with the conditions of growth from the gaseous phase and which was formed as a result of depositing a layer of $Al_xGa_{1-x}N$ (0<x≤1) on the bulk mono-crystalline GaN obtained in the supercritical solution, resistant to the conditions of growth from the gaseous phase.

The process of forming a template-type substrate from bulk mono-crystalline gallium-containing nitride is characterized in that in the autoclave, in the environment of a supercritical ammonia-containing solvent containing ions of alkali metals, gallium-containing feedstock is dissolved and gallium-containing nitride is crystallized from the supercritical solution on the surface of the seed from gallium-containing nitride at a temperature higher and/or pressure lower than that of the dissolution of the feedstock, and a layer of $Al_xGa_{1-x}N$ (0<x≤1) is deposited on the thus-obtained GaN layer, thus obtaining a template-type substrate with increased heat resistance, consisting of a layer of $Al_xGa_{1-x}N$ (0<x≤1) crystallized from a supercritical ammonia-containing solution and a layer of gallium-containing nitride crystallized from the gaseous phase, or a solution in liquid metal or metal mixtures, or from a solution in melted nitric metal compounds.

The process of obtaining a mixed template-type substrate from the bulk mono-crystal is characterized in that supercritical solution with a negative temperature coefficient of solubility of the gallium-containing nitride forms after the dissolution in a supercritical solvent containing ammonia and ions of alkali metals, and at least in the autoclave zone in which the seed was placed, by appropriately increasing the temperature or decreasing the pressure, a zone is created where the solution's solubility is supersaturated with respect to the seed and by controlling the concentration in such a way as not to cause spontaneous crystallization, selective crystallization of GaN occurs solely on the surface of the seed placed in the autoclave, and a layer of $Al_xGa_{1-x}N$, where $0<x\leq1$, is deposited on the thus-obtained GaN layer, resulting in the formation of a mixed template-type substrate from the mono-crystalline GaN/ $Al_xGa_{1-x}N$ ($0<x\leq1$).

The process according to claim 1 or 2 is characterized in that the degree of mixing of the x layer of $Al_xGa_{1-x}N$, deposited on the GaN layer, is $0<x\leq1$.

The process according to claim 1 or 2 is characterized in that a layer of $Al_xGa_{1-x-y}In_yN$ ($0\leq x<1$, $0\leq y<1$, $0\leq x+y<1$) with n-type electrical conductivity, doped with Si, is deposited on the complex template-type substrate by the growth method from the gaseous phase.

The template-type substrate, obtained by slicing with a wire saw of a gallium-containing nitride layer obtained by the method of growth from the gaseous phase, in accordance with Claim no. 4, with the thickness of over 3 mm.

Template-type substrate, according to the Claim no. 5, with high crystalline quality and with the dislocation density below $10^5/cm^2$.

The invention is illustrated in the enclosed figures:

Fig.1 presents the change in time of the temperature in the autoclave where p=const and shows the relation between the changes in the temperature and the dissolution and crystallization processes in the case of this invention; Fig.2 presents the change in time of the pressure in the autoclave where T=const and illustrates the relation between the changes in the pressure and the processes of dissolution and crystallization in the case of this invention; Fig.3 presents an axial intersection of the autoclave and the set of furnaces used for the purposes of this invention; Fig.4 presents a perspective diagram of the

apparatus used for obtaining bulk mono-crystalline gallium nitride; Fig.5 presents the relationship between the solubility of GaN in supercritical ammonia containing potassium amides (with Mineralizer: NH_3=0.07) and the pressure for T=400°C and T=500°C; finally, Fig.6 presents the change in time of the temperature in the autoclave for the purposes of this Example.

The first variant of this invention is based on an ammono-basic growth of the crystal and allows to obtain mono-crystalline gallium-containing nitride selectively deposited on the seed surface by creating chemical transport in a supercritical ammonia-containing solvent containing one or more mineralizers affecting its ammono-basic nature.

This process is characterized in that it allows to obtain a complex template-type substrate in the form of bulk mono-crystalline GaN/ $Al_xGa_{1-x}N$ (0<x≤1), in which the layer of $Al_xGa_{1-x}N$ (0<x≤1) was deposited on the GaN layer obtained by creating a supercritical solvent containing ammonia and ions of alkali metals in the autoclave, in which gallium-containing feedstock was dissolved and selective crystallization of the gallium-containing nitride was carried out from the solution on the seed's surface in the environment of a higher temperature and/or lower pressure than that of the dissolution process.

The key objective of the first variant is to perform selective crystallization on the seed's surface during the second process – crystallization. Therefore, the second variant of this invention concerns the process of crystallization of bulk mono-crystalline gallium-containing nitride, characterized in that it allows to obtain a bulk mono-crystalline template-type substrate with increased heat resistance, in which on the gallium-containing nitride layer a layer of $Al_xGa_{1-x}N$ (0<x≤1) was deposited by the growth method from the gaseous phase thanks to the fact that in the autoclave a supercritical solvent forms containing ammonia and ions of alkali metals in which the feedstock is dissolved, followed by selective crystallization of the gallium-containing nitride from the solution on the surface of the seed in the conditions of a higher temperature and/or lower pressure than that of the dissolution of the gallium-containing feedstock in a supercritical solvent.

Although in the second variant two zones are created simultaneously in the autoclave: the dissolution zone and the crystallization zone, it is advisable to control the supersaturation of the supercritical solution with respect to the seed by regulating the temperature of dissolution and the temperature of crystallization. Moreover, controlling of temperature would be easier if the temperature in the crystallization zone is set between

300 and 600°C, and the difference between the temperature in the dissolution zone and the crystallization zone in the autoclave is maintained below 150°C, preferably under 100°C. The supersaturation of the supercritical solution with respect to the seed can be regulated by placing one or more baffles in the autoclave to separate the dissolution zone (with low temperature) from the crystallization zone (with high temperature) and controlling the rate of the convection flow between those zones. Moreover, if the two zones are created in the autoclave: the dissolution zone and the crystallization zone, with an appropriate difference in temperature, the supersaturation of the supercritical solution with respect to the seed can be regulated by using the gallium-containing feedstock, supplied in the form of crystalline GaN whose total surface exceeds the total surface of the seed.

In the first variant alkali metal ions are introduced in the form of alkali metals and/or alkali metal compounds and/or their mixtures, particularly those not containing elements of Group XVII (halogens). Such ions of alkali metals may include one or more types selected from Li^+, Na^+, and K^+. It is particularly preferable to apply them in the form of alkali metals and their amides and azides in the molar ratio to ammonia between 1:200 and 1:2. The feedstock dissolved in the supercritical solution is gallium-containing nitride or a gallium precursor, which may form gallium compounds soluble in the supercritical solvent.

Although the process described in this invention is based on the reactions in a clear ammono-basic environment, application of feedstock in the form of GaN obtained through the HVPE method or another chemical method is also allowed, provided that chlorine or other elements of Group XVII do not negatively affect the environment in which the reaction occurs.

The feedstock can be gallium-containing nitride which undergoes a reversible process of dissolution in the supercritical ammonia-containing solvent. It can be also merged with metallic gallium which undergoes an irreversible reaction in the supercritical solvent.

The use of gallium nitride as gallium-containing nitride facilitates the control over the crystallization process. It is preferable to use the seeds from mono-crystalline GaN, although the following can also be used: GaN obtained through the HVPE method or the flux method, the seeds obtained through the high-pressure method, the seeds with A ($11\bar{2}0$), M ($1\bar{1}00$), or R ($1\bar{1}02$) surfaces cut out from the bulk mono-crystal obtained

from supercritical ammonia. For the purposes of the crystallization it is also possible to use the C (0001) surface having N-polarity.

In this invention, the processes of dissolution and crystallization are usually carried out at in parallel, and they are concurrently spatially separated in the autoclave. In other words, the supercritical ammonia-containing solvent is obtained in the autoclave, which contains ions of alkali metals. This solvent dissolves the gallium-containing feedstock, and crystallization of gallium-containing nitride is carried out from the supercritical solution on the surface of seed in the conditions of a higher temperature and/or lower pressure than that for the process of dissolution of the feedstock.

In the first variant it is recommended that the process of dissolving the gallium-containing feedstock be supplemented with a separate process of transferring the supercritical solution to a place with higher temperature and/or lower pressure. In this case, in the autoclave at least two zones with different temperature are simultaneously formed, and the gallium-containing feedstock is placed in the dissolution zone with low temperature while the seed is placed in the crystallization zone with high temperature. The difference in temperature between the dissolution zone and the crystallization zone should be set in such a way as to ensure chemical transport through the supercritical solution, which occurs mainly by convection. The difference in temperature between the dissolution zone and the crystallization zone exceeds 1°C, preferably between 5 and 150°C, and most preferably below 100°C.

Preferably, the gallium-containing nitride obtained in this invention has the formula of $Al_xGa_{1-x}N$, where $0<x\leq1$. The supercritical solvent is defined as follows: it contains NH_3 and/or its derivatives and a mineralizer in the form of ions of alkali metals, or at least ions of sodium or potassium. The feedstock consists primarily of gallium-containing nitride or its precursors selected out of the group including: azides, imides, amido-imides, amides, hydrides, metallic compounds and gallium-containing alloys, as well as metallic gallium. The definition of a precursor can be found further in this document.

In this invention, the seed contains at least a crystalline layer of gallium-containing nitride or other elements of Group XIII (IUPAC 1989). It is preferable that the surface dislocation density of that layer be lower than $10^6/cm^2$.

In this invention, crystallization of gallium-containing nitride can occur in the temperature between 100 and 800°C, preferably between 300 and 600°C, and most

preferably between 400 and 550°C. During crystallization of the gallium-containing nitride the pressure can range between 10 and 1000MPa, preferably between 100 and 550MPa, and most preferably between 150 and 300MPa.

The concentration of alkali metal ions in the supercritical solvent is regulated in such a way as to ensure proper solubility properties of the feedstock and the gallium-containing nitride, and the molar ratio of alkali metal ions to other species in the supercritical solvent is controlled in the range from 1:200 to 1:2, preferably between 1:100 and 1:5, and most preferably between 1:20 and 1:8.

In this invention, the growth of a mono-crystalline gallium-containing nitride is obtained by chemical transport in the supercritical solvent containing one or more mineralizers affecting its ammono-basic nature. Thus, this is the technique of ammono-basic crystallization, and the terms used in this invention should be understood in accordance with the following definitions:

Gallium-containing nitride is a chemical compound containing in its structure at least one atom of gallium and one atom of nitrogen, hence this is at least a binary compound – GaN, a ternary compound - AlGaN, InGaN or a quaternary compound AlInGaN, and composition of other elements in relation to gallium may be modified in its structure insofar as it does not collide with the ammono-basic nature of the crystallization technique.

Bulk mono-crystalline gallium-containing nitride means a mono-crystalline substrate in the form of gallium-containing nitride, on which opto-electronic devices may be obtained, such as: light-emitting diodes (LED) or laser diodes (LD) by the MOCVD method or by the methods of epitaxy growth such as HVPE.

Precursor of gallium-containing nitride is a substance or a mixture containing at least gallium, which may also contain alkali metals, elements of Group XIII (according to IUPAC 1989), nitrogen and/or hydrogen, and metallic gallium, its alloys or metallic compounds, hydrides, amides, imides, amido-imides and azides, which may form gallium compounds soluble in the supercritical ammonia-containing solvent as defined below.

Feedstock containing gallium is gallium-containing nitride or its precursor. Feedstock can be in the form of GaN obtained by flux methods, or a polycrystalline GaN

obtained from metallic gallium as a result of reaction in the supercritical ammonia-containing solvent.

Supercritical ammonia-containing solvent is a supercritical solvent consisting at least of ammonia, which contains one or more types of alkali metal ions, used for dissolution of gallium-containing nitride.

Mineralizer is a substance delivering one or more types of alkali metal ions to the supercritical ammonia-containing solvent, supporting dissolution of gallium-containing nitride.

Dissolution of the feedstock containing gallium is a reversible or irreversible process of formation, through the feedstock, of gallium compounds soluble in the supercritical solvent, for example gallium complexes. Gallium complexes are chemical complex compounds, in which a centrally placed gallium is surrounded by NH_3-type ligands or its derivatives NH_2^-, NH^{2-}.

Supercritical ammonia-containing solution is a solution obtained as a result of dissolution of the gallium-containing feedstock in the supercritical ammonia-containing solvent.

Solubility: Our experiences show that the state of equilibrium may be achieved between the solid, which is gallium-containing nitride, and the supercritical solution at sufficiently high temperature and pressure. Therefore, solubility of gallium-containing nitride may be defined as the equilibrium concentration of soluble gallium compounds obtained in the above mentioned process of dissolution of gallium-containing nitride. In this process, the equilibrium concentration, i.e. solubility, may be controlled by modifying the composition of a solvent, temperature and/or pressure.

Temperature and pressure coefficients of solubility: A negative temperature coefficient of solubility means that solubility is decreasing with temperature while all other parameters are constant. Whereas a positive pressure coefficient means that solubility is increasing with pressure while all other parameters are constant. Our research allows to state that solubility of gallium-containing nitride in the supercritical ammonia-containing solvent, at least in the temperature range between 300 and 550°C and the pressure in the range between 100 and 550MPa, shows a negative temperature coefficient and a positive pressure coefficient. That means, for example, that, as shown in Fig.1, after the feedstock

is dissolved in the autoclave under increased pressure maintained for 8 days at the level of 400°C (i.e., following the dissolution process), it is possible to obtain recrystallization of gallium nitride by increasing the temperature inside the furnace up to 500°C while maintaining the constant pressure of 200MPa (crystallization process). Whereas, as in Fig.2, after the feedstock is dissolved in the autoclave under increased pressure maintained for 2 days at 350MPa (i.e., following the dissolution process) it is possible to obtain recrystallization of gallium nitride by lowering the pressure down to 200MPa while maintaining the constant temperature of 500°C (crystallization process).

Supersaturation: If concentration of soluble gallium compounds in the supercritical ammonia-containing solution is higher than solubility of gallium-containing nitride in specific physico-chemical conditions, supersaturation of the supercritical ammonia-containing solution with respect to gallium-containing nitride in those conditions can be defined as the difference between the actual concentration and the solubility. While dissolving gallium-containing nitride in the closed system it is possible to obtain the state of supersaturation by, for example, increasing the temperature or decreasing the pressure.

Chemical transport of gallium-containing nitride in the supercritical ammonia-containing solution is a constant process involving dissolution of the gallium-containing feedstock in the supercritical solution, transport of soluble gallium compounds through the supercritical solution, as well as crystallization of gallium-containing nitride from the supersaturated supercritical solution. Generally, the driving force behind the chemical transport can be the difference in temperature, difference in pressure, difference in concentration, or chemical or physical differences between the feedstock being dissolved and the product of crystallization. The process according to this invention allows to obtain a bulk mono-crystalline gallium nitride as a result of the chemical transfer in the conditions of temperature difference, although it is necessary to maintain a higher temperature in the crystallization zone than in the dissolution zone.

Seed has been mentioned in the description above. Because it has crucial impact on the quality of the crystallized gallium-containing nitride, it is necessary to select a seed of the best possible quality. In particular, the selected seed should have homo-epitaxial surface with n-type electrical conductivity, e.g., Si-doped surface. Such seeds are obtained by growing gallium-containing nitrides from the gaseous phase (the HVPE or MOCVD methods), and the Si-doping during the growth process in the concentration between 10^{16}

and $10^{21}/cm^3$ gives them n-type electrical conductivity. Also, a composite seed can be used, in which an Si-doped GaN layer was deposited on the SiC-type (or similar) substrate, directly or through an AlN buffer layer.

Spontaneous crystallization from the supersaturated supercritical ammonia-containing solution means any undesirable process of nucleation and growth of the gallium-containing nitride crystals taking place at any site within the autoclave except at the surface of the seed. The definition also includes growth on the surface of the seed, in which the grown crystal has an orientation different from that of the seed.

Selective crystallization on a seed is the process of crystallization taking place on the surface of the seed in the absence of spontaneous crystallization, but also when the spontaneous crystallization occurs in negligible degree. This process is indispensable to obtain a bulk mono-crystal, which is, at the same time, one of the elements of this invention.

Temperature and pressure of the reaction: In the examples shown in this invention, temperature profile inside the autoclave was measured with use of an empty autoclave, thus without a supercritical ammonia-containing solution. Therefore, these are not the actual temperatures of the process carried out in supercritical conditions. The pressure was measured directly or was calculated on the basis of physico-chemical data of an ammonia-containing solvent for the assumed temperature of the process and autoclave volume.

Autoclave consists of a closed reaction chamber, in which crystallization is carried out in the ammono-basic environment in the range of temperature and pressure as mentioned above.

To implement the process according to the invention, it is preferable to use the apparatus shown on the diagrams in Fig.3 and Fig.4, described below in more detail.

The afore-mentioned process and the apparatus allow to obtain bulk mono-crystalline gallium-containing nitride. The bulk mono-crystal has low dislocation density (in the case of bulk GaN: $10^4/cm^2$) and thanks to the aluminum content it has increased heat resistance.

If gallium-containing nitride is deposited using the growth method from the gaseous phase, it would be preferable for the gallium-containing nitride, obtained in supercritical

ammonia, to have the form of $Al_xGa_{1-x}N$ (0<x<1) or to use bulk mono-crystalline $Al_xGa_{1-x}N$ (0<x<1) deposited on GaN. By Si doping of gallium-containing nitride during the growth from the gaseous phase it is possible to obtain $Al_xGa_{1-x-y}In_yN$ (0≤x<1, 0≤y<1, 0≤x+y<1) with n-type electric conductivity, and since it was crystallized on gallium-containing nitride obtained in supercritical ammonia in the conditions of growth from the gaseous phase it is possible to use it to create template-type substrate with high crystalline quality and the dislocation density below $10^5/cm^2$ with increased heat resistance.

A preferable example of this invention

The process according to this invention allows to separate the process of dissolving the feedstock from the process of transferring the supercritical solution to a higher temperature and/or lower pressure, wherein crystallization of gallium-containing nitride occurs on the surface of the seed. Moreover, the process comprises a step of simultaneous creation of at least two zones with different temperature in the autoclave, whereas the gallium-containing feedstock is placed in the dissolution zone with a lower temperature and the seed being placed in the crystallization zone with a higher temperature. The difference in temperature between the dissolution zone and the crystallization zone is controlled in such a way as to ensure chemical transport through the supercritical solution by way of convection, with the difference in temperature between the dissolution zone and the crystallization zone exceeding 1°C. The gallium-containing nitride obtained in the supercritical ammonia has the form of $Al_xGa_{1-x}N$, where 0≤x<1, while the gallium-containing nitride obtained from the gaseous phase has the form of $Al_xGa_{1-x-y}In_yN$, where 0≤x<1, 0≤y<1, 0≤x+y<1 and may contain donor-type, acceptor-type or magnetic-type dopants. NH_3, containing alkali metal ions and/or its derivatives, may serve as the supercritical solvent. The feedstock mainly consists of gallium-containing nitride or its precursors selected out of the group consisting of azides, imides, amido-imides, amides, hydrides, metallic compounds and gallium-containing alloys, as well as metallic gallium. The seed contains at least a crystalline layer of gallium-containing nitride or other elements of Group XIII (according to IUPAC, 1989).

Crystallization of gallium-containing nitride occurs at the temperature from 100 to 800°C and under pressure from 10 to 1000MPa, while the content of alkali metal ions in the supercritical solvent is controlled in such a way as to ensure proper solubility of the

feedstock and gallium-containing nitride. The molar ratio of alkali metal ions to other species in the supercritical solvent is controlled in the range from 1:200 to 1:2.

The performed measurements showed that the best obtained bulk mono-crystalline GaN can have a dislocation density below $10^4/cm^2$ with simultaneous half width of the X-ray rocking curve from (0002) plane below 60 arcsec, which guarantees the proper quality and life of the manufactured semiconductor devices. At the same time, due to the electrical conductivity of the substrate, it is possible to deposit on it an n-type pad electrode.

GaN shows good solubility in the supercritical NH_3 provided that alkali metals or their compounds, such as KNH_2, are introduced into it. The diagram in Fig.5 presents GaN solubility in a supercritical solvent in the function of pressure for the temperature 400 and 500°C, with solubility being defined as the molar ratio: $S_m \equiv GaN^{solution}:(KNH_2+NH_3) \times 100\%$. In the presented example, the solvent is in the form of KNH_2 solution in the supercritical ammonia with the molar ratio of $x \equiv KNH_2:NH_3$ equal to 0.07. It should be expected that solubility S_m is a smooth function of temperature, pressure, and mineralizer's content, expressed by the equation $S_m \equiv S_m(T,p,x)$. Infinitesimal changes of S_m can be expressed as follows:

$$\Delta S_m \approx (\partial S_m/\partial T)_{p,x} \Delta T + (\partial S_m/\partial p)_{T,x} \Delta p + (\partial S_m/\partial x)_{T,p} \Delta x,$$

where the partial derivatives $(\partial S_m/\partial T)_{p,x}$, $(\partial S_m/\partial p)_{T,x}$, $(\partial S_m/\partial x)_{T,p}$ specify the behavior of S_m with changes in particular parameters. In this description those derivatives are called „coefficients" (e.g., $(\partial S_m/\partial T)_{p,x}$ is referred to as "the temperature coefficient of solubility").

Fig.5 shows that the solubility is increasing with pressure and decreasing with temperature. Those relationships allow us to obtain bulk mono-crystalline gallium-containing nitride through its dissolution in the higher-solubility conditions and its crystallization in the lower-solubility conditions. The negative temperature coefficient means that in the presence of a temperature gradient, the chemical transport of gallium-containing nitride will occur from the dissolution zone with a lower temperature to the crystallization zone with a higher temperature. It turned out that other gallium compounds, even metallic gallium, may also be the source of ammonia complexes of gallium. For example, gallium complexes of the composition specified above can be introduced into a solvent based on the simplest substrate, such as metallic gallium. Next, by appropriately modifying the conditions (e.g., by raising the temperature) it is possible to obtain a solution

supersaturated with respect to gallium-containing nitride as well as crystallization on the seed. The process according to this invention allows to obtain growth of bulk mono-crystalline gallium-containing nitride on the seed and leads in particular to the creation of stoichiometric gallium nitride obtained in the form of a bulk mono-crystalline layer on a gallium-nitride seed. Since such a mono-crystal is obtained in a supercritical solution containing alkali metal ions, it also contains over 0.1ppm of alkali metals. Because it is preferable to maintain the purely basic nature of the supercritical solution (mainly in order to avoid corrosion of the apparata), halides are purposefully not introduced into the solvent. The process according to this invention also allows us to purposefully substitute from 0.05 to 0.5 Ga with Al. The possibility to smoothly change the composition results in the ability to control the lattice constant of the obtained nitride. Moreover, the bulk mono-crystalline GaN can receive donor-type dopants (e.g., Si, O) and/or acceptor-type dopants (e.g., Mg, Zn) and/or magnetic-type dopants (e.g., Mn, Cr) in the concentrations of between 10^{17} and $10^{21}/cm^3$. Those dopants modify the optical, electric, and magnetic properties of gallium-containing nitride. With regard to other physical properties, the bulk mono-crystalline gallium nitride being obtained has the surface dislocation density below $10^6/cm^2$, preferably below $10^5/cm^2$, and most preferably below $10^4/cm^2$. Moreover, its half width of the X-ray rocking curve from (0002) plane is below 600 arcsec, preferably below 300 arcsec, and most preferably below 60 arcsec. The best obtained bulk mono-crystalline gallium nitride may have the defect density below $10^4/cm^2$ and at the same time the half width of the X-ray rocking curve from (0002) plane below 60 arcsec (for Cu K α_1).

The apparatus used for obtaining a bulk mono-crystal is shown in Fig.3 and Fig.4. The basic unit of the apparatus is the autoclave 1 for obtaining a solvent in a supercritical state, equipped with the installation 2 for providing chemical transport through the supercritical solution inside the autoclave 1. The autoclave 1 is placed in the chamber 3 of a set of two furnaces 4 equipped with heating 5 and/or cooling devices 6 and secured in the desired position with respect to the furnaces 4 by means of the screw-type blocking device 7. The furnaces 4 are mounted on the bed 8 and secured with steel bands 9 wrapped around the furnaces 4 and the bed 8. The bed 8 together with the set of furnaces 4 is mounted rotationally in the base 10 and secured at a desired angle by means of the pin interlock 11, allowing to control the rate and type of the convection flow in the autoclave 1. In the autoclave 1 placed in the set of furnaces 4 the convention flow of the supercritical solution occurs, controlled by the installation 2 in the form of the horizontal baffle 12 occupying

over 70% of the cross-section of the autoclave, separating the dissolution zone **13** from the crystallization zone **14** in the autoclave **1**. The horizontal baffle **12** is placed around the middle of the length of the autoclave. The temperature level of particular zones in the autoclave **1**, within the range of temperature between 100 and 800°C, is set in the furnaces **4** by means of the control device **15**. In the autoclave **1** the dissolution zone **13** coinciding with the low-temperature zone of the furnace system **4** is located above the horizontal baffle (or baffles) **12** and the feedstock **16** is added into said zone **13**. The feedstock is introduced in the amount of no more than 50% of the volume of the dissolution zone. The feedstock in the form of metallic gallium is introduced into the crucible in such amount so that its volume should not occupy more than 80% of that of the dissolution zone. The crystallization zone **14** coincides with the high-temperature zone of the furnace set **4** and is located below the horizontal baffle (or baffles) **12**. The seed **17** is placed in this zone. The location of the seed **17** is below the intersection of the rising and falling convection streams, slightly above the furnace's bottom. The zone in which the installation **2** regulating the convection flow is located is equipped with the cooling device **6**. Thus, a difference in the temperature occurs between the dissolution zone **13** and the crystallization zone **14**. At the level of the bottom of the crystallization zone the cooling device **18** is located, allowing the zone to rapidly cool off after the completion of the process and significantly preventing dissolution of the crystal during the furnace's cooling-off period following the crystallization process.

Thus obtained bulk mono-crystalline gallium nitride can have the dislocation density below $10^5/cm^2$ and the half width of the X-ray rocking curve from the plane below 60 arcsec. After slicing it into wafers with a wire saw with an off-angle between 0.05 and 0.2 degree with respect to the principal axis of the crystal, in those conditions it is possible to add to them, by the HVPE method, 3mm of GaN with n-type electrical conductivity by maintaining the growth rate of $30\mu m/h$ for 100 hours.

Thus obtained bulk mono-crystalline GaN with the width of 5mm is sliced for 25 hours with a wire saw into 0.5mm thick wafers. In this manner, it is possible to obtain at least 4 substrates. Those substrates, apart from the high crystalline quality, also have electrical conductivity, so they can be used as substrates for opto-electronic devices made on the basis of semi-conductors, such as laser diodes.

Example

In the high-pressure autoclave **1** with the diameter of 40 mm, length 480 mm and the volume of 600cm^3 (Fig.6), 53.0g of feedstock was placed in the crucible in the dissolution zone **13** in the form of metallic gallium, and in the crystallization zone **14** a 1-inch, 2.0g seed was placed in the form of GaN obtained by the HVPE method. 12.0g of metallic sodium of the purity 4N and 19.5g of 4N metallic potassium were added as the mineralizer. Then 255.0g of ammonia (5N) was introduced to the autoclave **1** and the autoclave was tightly closed. The autoclave **1** was then placed in the furnace system **4** and heated up to the temperature of 200°C. After 3 days the temperature was raised to 450°C. The pressure inside the autoclave was approximately 230MPa. In this way, supercritical ammonia-containing solution was obtained with the following molar ratio: $KNH_2 : NH_3 = 0.035$; $NaNH_2 : NH_3 = 0.035$.

After 1 day the temperature in the dissolution zone **13** was lowered to 370°C, and the temperature in the crystallization zone **14** was raised to 500°C. In those conditions, the autoclave **1** was left unchanged for the next 20 days (Fig.6). As a result of the process, the feedstock in the dissolution zone **13** was partly dissolved and crystallization of gallium nitride occurred on the HVPE seed in the crystallization zone **14**. The total thickness of the mono-crystalline layer on both sides of the seed was approximately 5mm.

Thus obtained crystal was subjected to the following processes in order to use it as a substrate:

1) The 5mm mono-crystalline layer deposited on the seed with HVPE-GaN was placed in the furnace and subjected to annealing for between 1 to 5 hours in the nitrogen atmosphere containing low amounts of oxygen and in the temperature between 600°C and 900°C.

2) Next, the sample was then placed on a wire saw manufactured by the Takatori Corp. The sample was situated at an angle below 1 degree in order to give it the proper off-angle with respect to the principal axis of the crystal. The sample was then sliced into 5 wafers using a wire saw, thus obtaining samples with the off-angle of between 0.05 and 0.2 degrees.

3) Next, the samples were placed in the furnace and again subjected to annealing for between 1 and 5 hours in the nitrogen temperature containing low amounts of oxygen and in the temperature between 600°C and 900°C. (Thus prepared samples are called: GaN substrates)

4) Next, GaN substrates were mounted on worktables, placed into a polishing machine manufactured by Logitech Ltd. and polished consecutively on both sides. In the polishing process diamond tools as well as silica, or alumina slurries (with pH from 3 to 6 or else from 9 to 11) were used. The roughness of the obtained surfaces was lower than 10Å.

5) A protective GaN or AlGaN layer (several-micron thick) was then added to the surface of the GaN substrate using the HVPE method in the below specified conditions, thus obtaining the template-type substrate. The conditions of the HVPE process were as follows: reaction temperature: 1050°C, reaction pressure: atmospheric (0.1Mpa), partial ammonia pressure: 0.03MPa, partial pressure $GaCl_3$: 100Pa, hydrogen carrier gas.

6) Alternatively, on the GaN substrate with the afore-described protective layer, or on the GaN substrate without the protective layer, a 3mm-thick GaN layer was created using the HVPE method. After slicing and polishing in accordance with the afore-described methods a 0.5mm-thick template-type substrate was obtained for use in opto-electronic devices.

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I/03 - 100840

Claims

1. The process of forming a template-type substrate from bulk mono-crystalline gallium-containing nitride, characterized in that in the autoclave, in the environment of a supercritical ammonia-containing solvent containing ions of alkali metals, gallium-containing feedstock is dissolved and gallium-containing nitride is crystallized from the supercritical solution on the surface of the seed from gallium-containing nitride at a temperature higher and/or pressure lower than that of the dissolution of the feedstock, and a layer of $Al_xGa_{1-x}N$ ($0<x\leq1$) is deposited on the thus-obtained GaN layer, thus obtaining a template-type substrate with a increased heat resistance, consisting of a layer of $Al_xGa_{1-x}N$ ($0<x\leq1$) crystallized from supercritical ammonia-containing solution and a layer of gallium-containing nitride crystallized from the gaseous phase, or a solution in liquid metal or metal mixtures, or from a solution in melted nitric metal compounds.

2. The process for obtaining a composite template-type substrate from bulk monocrystal, characterized in that supercritical solution with a negative temperature coefficient of solubility of gallium-containing nitride forms after the dissolution in a supercritical solvent containing ammonia and ions of alkali metals, and at least in the autoclave zone in which the seed was placed, by appropriately increasing the temperature or decreasing the pressure, a zone is created where the solution's solubility is supersaturated with respect to the seed and by controlling the concentration in such a way as not to cause spontaneous crystallization, selective

crystallization of GaN occurs solely on the surface of the seed placed in the autoclave, and a layer of $Al_xGa_{1-x}N$, where $0<x\leq1$, is deposited on the thus-obtained GaN layer, resulting in the formation of a composite template-type substrate from the mono-crystalline GaN/ $Al_xGa_{1-x}N$ ($0<x\leq1$).

3. The process according to claims 1 and 2, characterized in that the level of intermixing of the x layer of $Al_xGa_{1-x}N$, deposited on the GaN layer, is $0<x\leq1$.

4. The process according to claims 1 and 2, characterized in that a layer of $Al_xGa_{1-x-y}In_yN$ ($0\leq x<1$, $0\leq y<1$, $0\leq x+y<1$) with type-n electric conductivity, doped with Si, is deposited on the composite template-type substrate by the growth method from the gaseous phase.

5. The template-type substrate obtained by slicing with a wire saw of a gallium-containing nitride layer obtained by the method of growth from the gaseous phase, according to claim 4, with the thickness of over 3 mm.

6. The template-type substrate according to claim 5, with high crystalline quality with the dislocation density below $10^5/cm^2$.
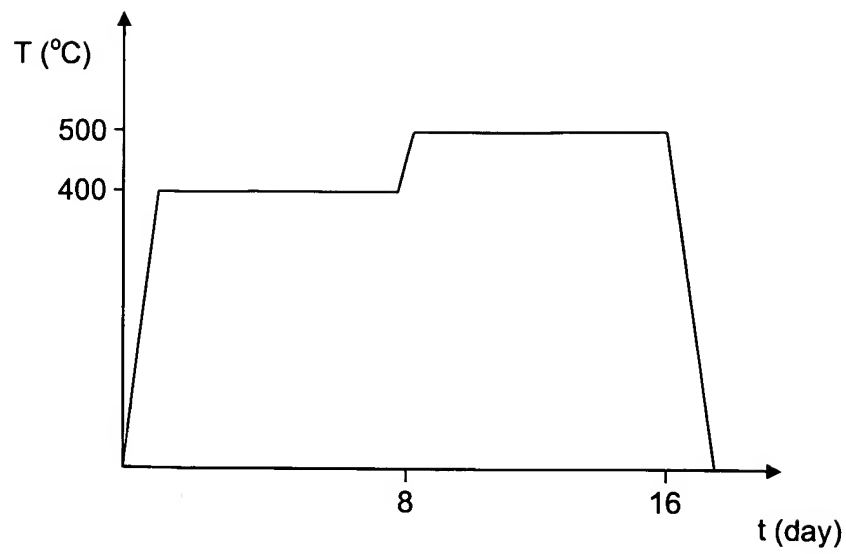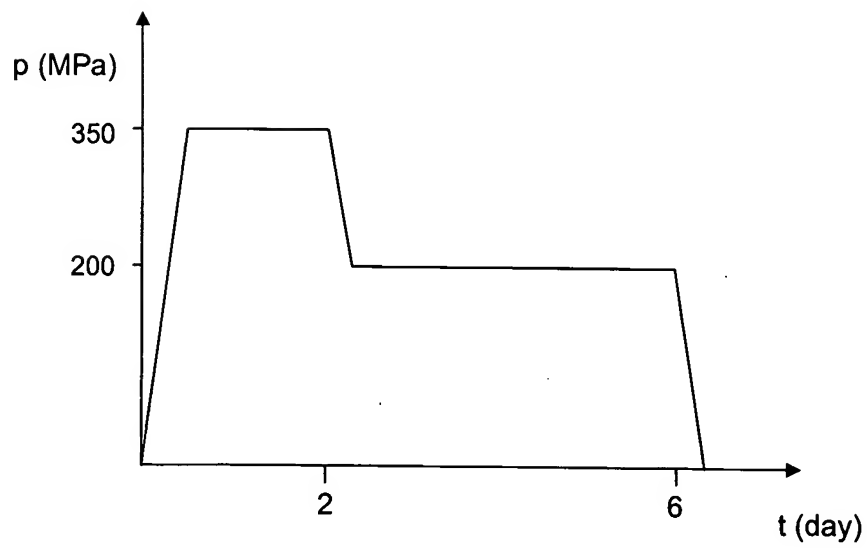
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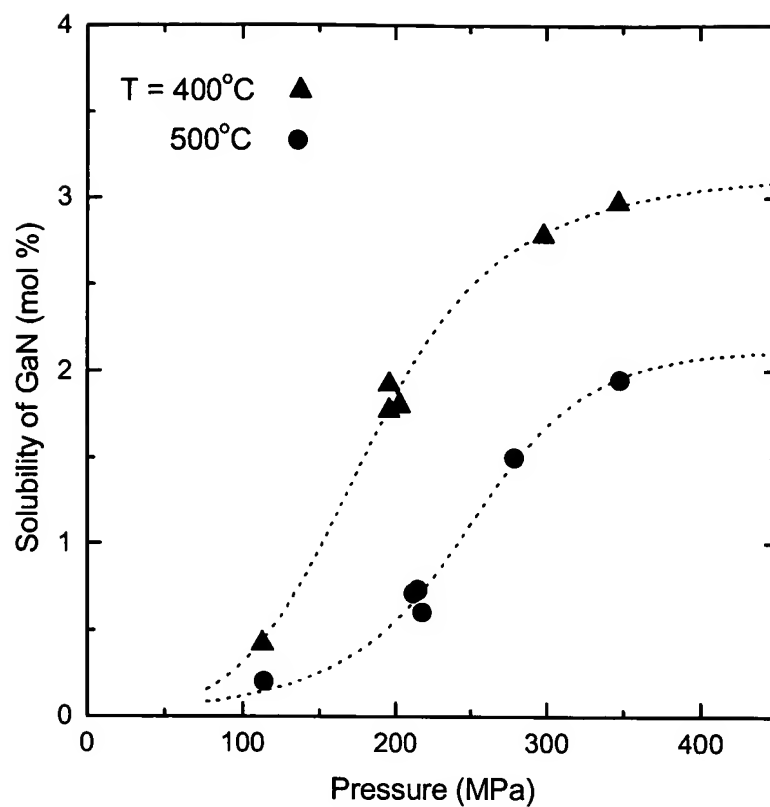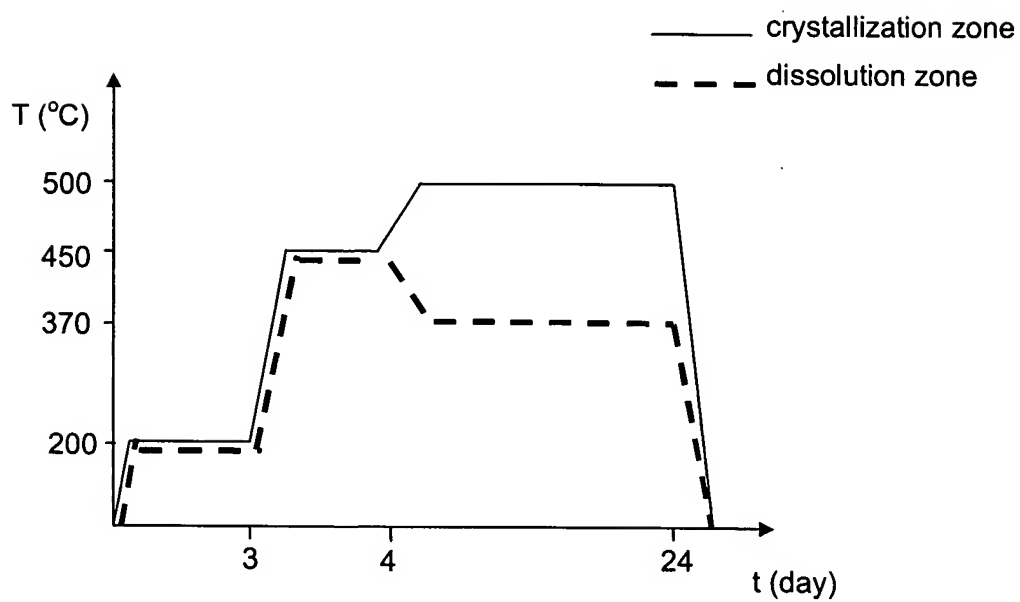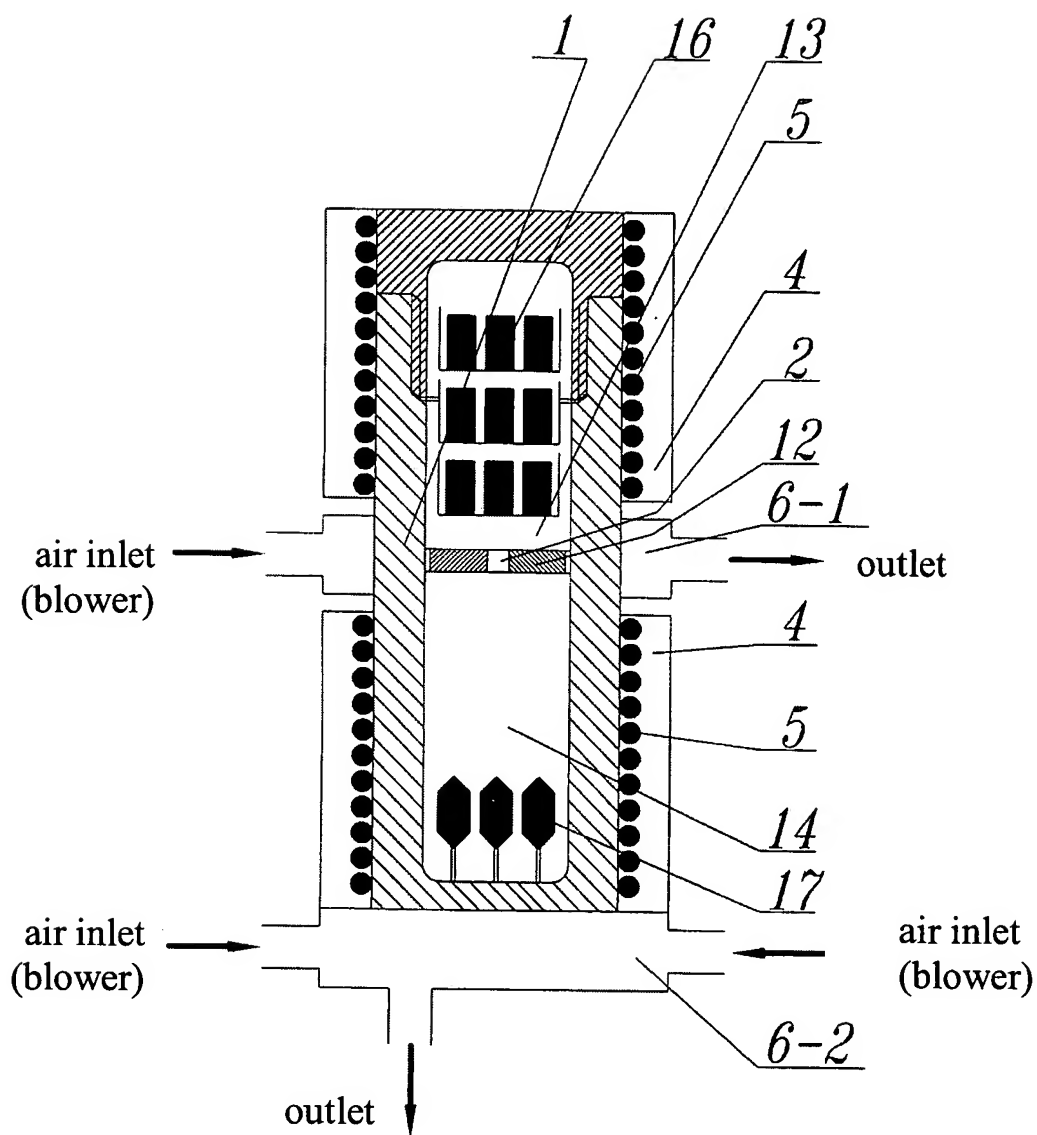Ewa Malewska
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Fig. 1

Fig. 2

Fig. 5

Fig. 6

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air inlet
(blower)

outlet

air inlet
(blower)

air inlet
(blower)

outlet
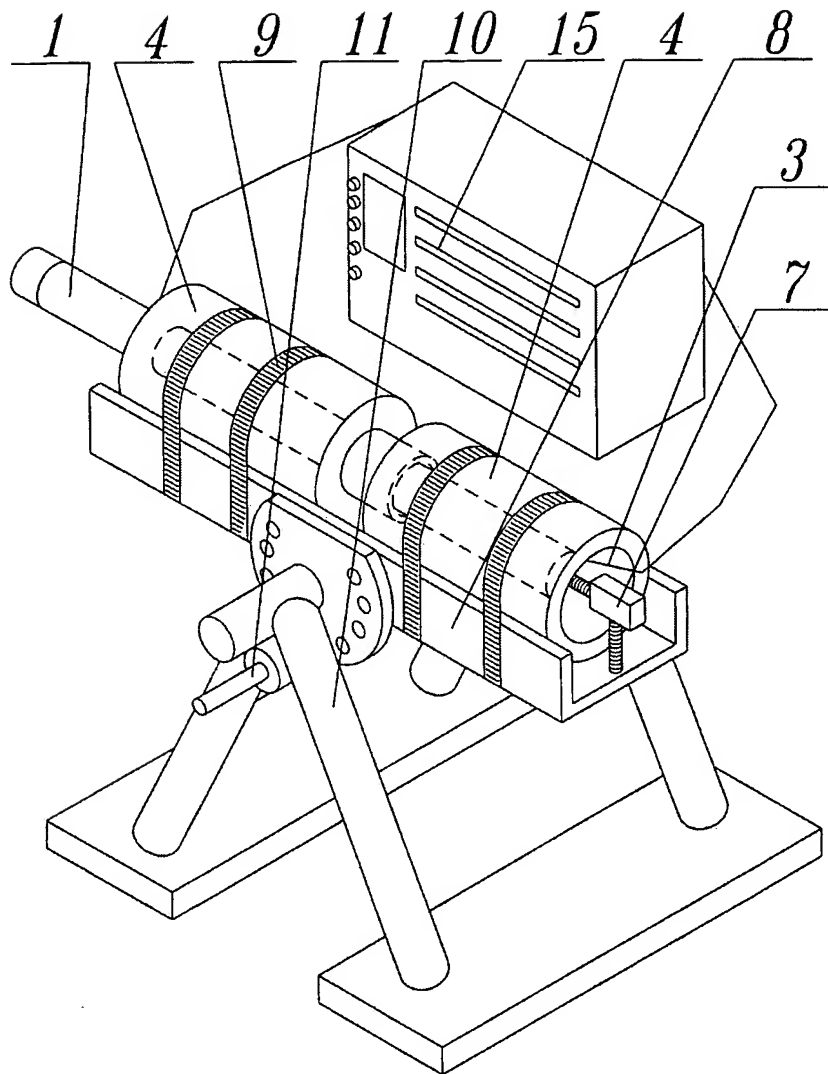
Fig. 3

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1 4 9 11 10 15 4 8

3

7

Fig. 4

I/03-100840

List of reference numerals:

1 – autoclave

2 – installation controlling convection flow

3 – chamber of a set of furnaces

4 – set of furnaces

5 – heating devices

6 – cooling devices

7 – screw-type blocking device

8 – bed

9 – steel tapes

10 – base

11 – pin interlock

12 – horizontal baffle

13 – dissolution zone

14 – crystallization zone

15 – control system

16 – feedstock

17 – seed

18 – cooling device

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